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Carbon Dioxide (CO_2) Separation from Natural Gas using Single-layer and Dual-layer Mixed-matrix Membranes (MMMs)

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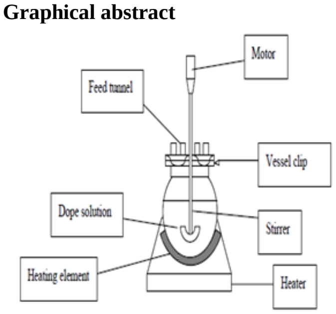
Graphical abstract



Abstract

The present research investigated the utilizing of single and dual-layer flat sheet mixed-matrix membranes (MMMs) for carbon dioxide (CO_2) separation. In this research, zeolite 4A is incorporated into a processable polymeric material, polyethersulfone (PES) of MMMs to get the high selectivity and permeability of membrane. Single-layer flat sheet MMMs have been successfully fabricated by adjusting the weight percent of zeolite loading in total solid as the effect of zeolite loading on the performance of MMMs were investigated. It shows that the higher the zeolite loadings, the higher the CO_2/CH_4 selectivity which is from 1.54 at 0wt % zeolite loading to 3.20 at 20wt % zeolite loading. Besides that, dual-layer flat sheet MMMs was also successfully fabricated with blending of PES and zeolite as selective top-layer and neat PES as sub-layer. Comparison of the results of permeability and selectivity between single and dual layer MMMs with same zeolite loading were studied. The performance of these newly developed dual-layer flat sheet of MMMs gives the best result with CO_2/CH_4 selectivity for dual layer MMMs is 9.63, tripled of the selectivity of single layer MMMs, 3.20.

Keywords: Mixed-matrix; membrane; dual-layer flat sheet; gas separation; selectivity

1.0 INTRODUCTION

Separation of CO_2/CH_4 using membrane has received great attention due to the variety in industrial applications such as natural gas purification and CH_4 recovery from landfill gas. For instance, the removal of carbon dioxide from the natural gas is required before it can be distributed to the consumers, since CO_2 can be very corrosive towards the gas pipe lines [1]. Therefore, separation of CO_2 and CH_4 is necessary in this process. In order to extend the membrane application and compete successfully with the existing CO_2/CH_4 gas separation technologies, great attention has been paid in fabricating membrane with high separation performance that possess high selectivity and permeability outcomes [2]. In fact, these two parameters; flux or permeability and selectivity are greatly determined the performance of the membrane material. Flux is the volumetric (mass or molar) flow rate of fluid passing through the membrane per unit area per unit time and also known as permeation rate. Meanwhile, selectivity is a measure of the relative permeation rates of various components through the membrane [3]. Membranologists nowadays also are noticed to seek more robust membrane materials in order to fabricate membrane that can withstand aggressive environments.

Current polymeric membrane materials have already reached the tradeoff limit between selectivity and permeability [4]. In other words, pure polymer membranes had reached the limit such as high temperature instability, low selectivity, and swelling and decomposition in organic solvents. On the other hand, the presence of inorganic material such as zeolites had shown very attractive permeation properties with significantly better permeation rate and selectivity than pure polymeric materials without zeolites [5]. Therefore, in this research study, mixed-matrix membrane has been proposed as an alternative approach by incorporating zeolites into the processing of polymeric polymer with dual-layer of mixed-matrix membranes (MMMs) in order to achieve high selectivity and permeability of membrane. Polyethersulfone (PES) is chosen as the polymer due to its high mechanical strength and low cost of material.

Another significant factor that affects the performance of membrane is the morphology or the micro-structure of the membrane. Lin *et al.*, [6] stated that membrane with asymmetric structure yield an outstanding performance in gas separation application as a result of formation of thin and dense selective layers supported by thick and porous sub-layers. The skin or top layer (0.1 to 5 mm) is responsible for the membrane selectivity whereas, the support or porous layer (50 to 150 mm) offers to improve the porosity and gas permeability. Fabrication of single-layer wholly integrated asymmetric either flat sheet or hollow fibre membrane involve high manufacture cost, so, dual-layer membranes is introduced to meet the reduced cost [7].

This is proven by Widjojo *et al.*, [8] that mentioned the fabrication of dual-layer membrane maximizes the functionality of expensive material such as zeolite. Thus, this study outlines the fabrication of a dual-layer flat sheet membrane with a novel design of mixed-matrix, composed of two layers which are made of blends of mixed-matrix materials which are polyethersulfone (PES) and zeolite as top layer (TL) and PES as support-layer (SL). Objectives of this study are to investigate the effect of zeolite loading on the performance of MMMs produced in terms of permeability and selectivity of CO_2 and CH_4 separations and to compare the results of permeability and selectivity between single and dual layer MMM.

2.0 EXPERIMENTAL

2.1 Materials

Selection of membrane material is the key factor to determine the performance of dual-layer flat sheet membrane. It covers for the selection of polymer, inorganic loader and organic solvent.

2.1.1 Materials PES as Polymer Material

Polymer that has been chosen was polyethersulfone (PES) which is known for its toughness and stability at high temperatures. Polyethersulfone (PES) is a heat-resistant, amorphous, transparent and pale amber high performance thermoplastic with T_g of about 215ºC.

2.1.2 Zeolite

Zeolite is crystals that characterized by a three-dimensional pore system, with pores of precisely defined diameter. This study used zeolite type 4A due to its appropriate pore size opening (3.8Å) which in between of carbon dioxide and methane molecules sizes makes it enable to discriminate the molecules. As zeolite 4A only allows smaller molecules to pass through makes the separation between these molecules can be achieved [9].

2.1.3 DMAc Solvent

Dimethylacetamide is an organic compound with the formula $CH_3C(O)N(CH_3)_2$. DMAc has high chemical and thermal stability and is completely miscible with water at all temperatures. Hence, DMAc was chosen due to its high solvency, high boiling point and good chemical stabilities.

2.2 Dope Solution Preparation

Zeolite powders were dried in a vacuum condition of 250ºC at least three hours before used to remove the adsorbed water vapor or other organic vapors. Prior to the preparation of the dope solution, all the equipments needed were dried in oven to remove moisture content. The materials such as PES and zeolite-4A, and the solvent, dimetylacetamide (DMAc) were weighed based on the desired value. The composition for the mixed matrix top layer dope solution was PES, DMAc and different zeolite 4A loading in total solid while the composition for the sub-layer dope solution was PES and DMAc. Table 1 depicts the composition of PES, zeolite and NMP used in dope solution.

The preparation process was slightly different from the neat polymer dope solution. For top layer membrane, firstly, zeolite was dispersed in the solvent in a round bottom reaction vessel stirred by motor driven stirrer as shown in Figure 1 for around 3 hours at a high speed to force particles to separate homogenously. Secondly, a desirable amount of PES was added gradually into the zeolite/solvent mixture and stirred to allow uniform mixing and form the homogenous polymer solution. Thirdly, the PES/zeolite/DMAc mixture was leaved for a night under the continuous but slow stirred to remove the air trapped around the zeolite surface, which may exacerbate the formation of voids between polymer and zeolite phases. For sub-layer membrane, PES was added gradually into the solvent and stirred. The PES/DMAc mixture was leaved overnight under stirring condition in order to acquire a homogeneous mixture.

2.3 Fabrication of Single and Dual-Layer Flat Sheet MMMs

After a homogeneous solution was obtained, the solutions were degassed for 90 minutes. Dry/wet phase inversion technique was applied in order to produce asymmetric membrane. The casting technique has been done manually. Firstly, about 10 ml of dope solution was poured onto a clean glass plate. Then, glass rod used to spread the solution was dragged backward gently for 10seconds. Membranes were cast at different thickness by varying the thickness of masking tape attached at the glass plate. After that, the glass plate with the membrane film was then immersed into the coagulant bath or water bath. The membrane was immersed in the coagulant bath for one day and finally was air-dried for one day before stored in a sealed plastic bag prior testing. Unlike single-layer of membrane fabrication, dual-layer membrane needs to co-cast the sub-layer dope solution above the top-layer film.

Table 1 Composition of PES, zeolite and NMP used in dope solution

Dope Solution	Materials	Weight Percent	Zeolite Loading in Total Solid	
1	Zeolite	40 %	10%	20%
	PES		90%	80%
	DMAc	60 %	-	-
2	PES	25%	-	-
	DMAc	75%	-	-

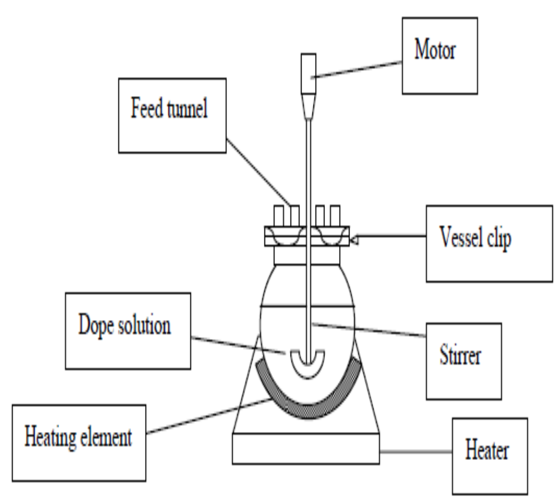


Figure 1 Preparation set up for membrane dope solution

2.4 Fourier Transform Infrared (FTIR) Spectroscopy

Molecular orientation of flat sheet membranes was measured using FTIR spectroscopy since the preferred orientations of specific functional groups can be easily and visibly determined. Samples of membranes about 5 cm^2 were mounted at a position with skin surface facing infrared beam and were rotated according to shear direction. A spectrum of linear dichroism was then obtained by a straightforward subtraction of plane polarized infrared spectra perpendicular to shear direction from plane polarized infrared spectra parallel to shear direction. Samples of membranes about 5 cm^2 were mounted at a position with skin surface facing infrared beam and were rotated according to shear direction. A spectrum of linear dichroism was then obtained by a straightforward subtraction of plane polarized infrared spectra perpendicular to shear direction from plane polarized infrared spectra parallel to shear direction.

2.5 Field Emission Scanning Electron Microscopy (FESEM)

FESEM is one of techniques used in this study to characterize the PES-Zeolite/PES dual-layer flat sheet membrane and several of single layer flat sheet membranes produced. It was used to determine the morphology of the membranes produced. Membranes samples will be freeze-fractured using liquid nitrogen and coated with a thin layer of gold using an SPI-Module sputter. The cross-section and membrane surface of the flat sheet membranes will be examined using FESEM.

2.6 Gas Permeation Test

The permeation property of the fabricated membranes involves the use of gas permeation cell by which the membrane was fixed on the cell and pressurized at the feed side. Gas permeation rates were measured by a soap bubble flow meter. The membrane sample was placed in the lower part of the permeation cell. The upper part was then being clamped with the lower part and sealed tight with a rubber O-ring. The feed gas was introduced through upper chamber and the permeate stream will emerge from the membrane sheet and flowed out from the lower chamber to the bubble soap flowmeter.

Permeability of pure gas was performed at 35ºC with pressure up to 7bar and measured three times for each membrane sample and was determined by measuring the constant volume of permeate and the required time for permeate to reach the volume. Pure CH_4 and CO_2 are used as the test gases.

■3.0 RESULTS AND DISCUSSION

3.1 FTIR Spectroscopy Analysis for Molecular Orientation of Mixed-Matrix Membrane

Spectra were collected from the neat polyethersulfone (PES) membrane and the blends of polyethersulfone and zeolite membrane. Polymer-zeolite samples contained 20wt % zeolite. Figure 2 shows the FTIR spectra for the membranes in the 450-4000 cm^{-1} wave number range. The pure PES is the bottom spectrum and the zeolite-PES blend is the top spectrum. The transmittances of the spectra were below 75% throughout the entire spectrum. Overall, there is no difference between the spectra of neat PES membrane and blends of PES-zeolite membrane. Hence, it shows that even zeolite was load to the membrane; it does not change the interaction of polymer. Functional group of PES is same even after the addition of zeolite. Functional group that was analysed by FTIR spectroscopy is the free –OH groups which appearing at around 3447 cm^{-1}. This produces a broad –OH band from 3100 to 3800 cm^{-1}. Peaks below 3000 $cm^{-1}$are associated with C-H stretches. Investigating the lower region of the IR spectrum also provides some insight into the functional group of the membranes. It shows the FTIR region between 1800-1550 cm^{-1} for all two systems and the spectrum shows the aromatic C-C stretches present in the spectra at 1637 cm^{-1}.

3.2 FESEM Analysis for Single and Dual Layer Flat Sheet of MMMs Formation

PES-zeolite membrane is successfully fabricated with 20wt % of zeolite loading of total solid. As shown in Figure 3a, the structure of single-layer MMM comprises of selective dense layer and porous support layer. The finger-like structures are thinner and longer compared to the finger-like structures of flat sheet dual-layer (as shown in Figure 4a). Figure 3b depicts that the void entrances are big enough for the gas to enter the membrane. White particles shown in the figures are zeolite 4A. The zeolites are dispersed uniformly throughout the membrane and not accumulated each others.

This study also discovers for the feasibility to fabricate the new design of mixed-matrix dual-layer flat sheet membrane which comprises of blending of PES-Zeolite as top layer while neat PES as sub-layer. The top layer will be function as selective dense skin layer and the sub-layer will provide the mechanical support for the top layer as shown in Figure 4a. The zeolites are dispersed uniformly in the selective top layer of flat sheet dual-layer of MMM. However, Figure 4b illustrates that zeolites are not very compatible with polymer PES because there are large empty space between pores and zeolites.

The difference between single and dual-layer MMMs is the place of dispersion of zeolites 4A. For single-layer MMM, the zeolites were dispersed uniformly throughout membrane. In fact, the zeolites were present either in selective layer or support layer while, for dual-layer MMMs, the zeolites are only present in selective dense layer.

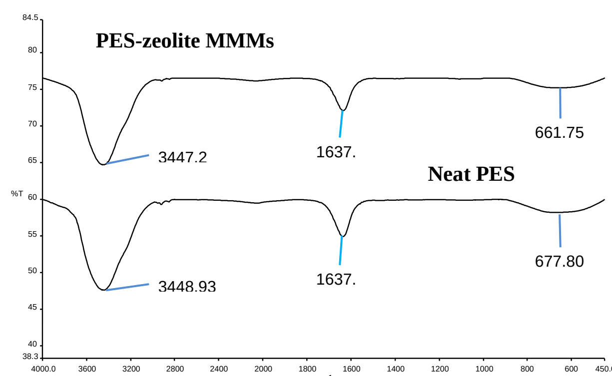


Figure 2 FTIR spectroscopy results for PES-zeolite MMM at zeolite loading 10wt% and neat PES membrane

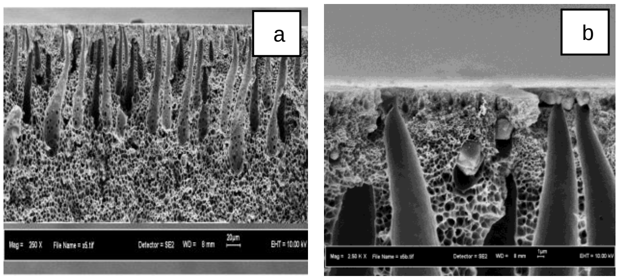


Figure 3 FESEM photos of casting using PES-zeolite (20wt% of zeolite loading), a) cross-section of single-layer membrane, b) zeolite loading in selective layer of single-layer membrane

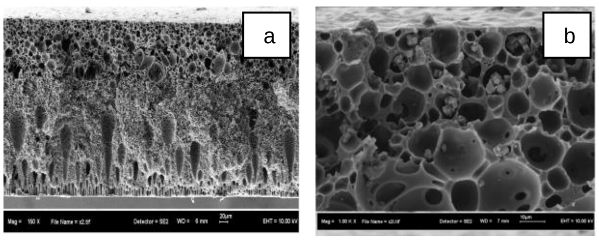


Figure 4 FESEM photos of co-casting using PES-zeolite/PES (20wt% of zeolite loading), a) cross-section of dual-layer membrane, b) zeolite loading in selective layer of dual-layer membrane

3.3 Effect of Zeolite Loading on Carbon Dioxide and Methane Separation Performance of Single Layer MMMs

Overall, there are observed that MMMs with 20wt % zeolite depicted the highest selectivity but the lowest permeability while MMMs with 10wt % zeolite showed good and quite high selectivity and permeability for the gases separation performance. Selectivity for neat PES is very low about 1.5 but have the highest permeability as shown in Table 2.

The permeability of both gases decreases with an increase in zeolite content for PES–zeolite MMMs. This decreasing trend of gas permeability with zeolite loading may be easily understandable because of both polymer chain rigidification and partial pore blockage of zeolites may lead to lessen in the gas permeability of MMMs [10].

Besides that, this study exhibits that CO2/CH4 selectivity of PES–zeolite MMMs increases with an increase in zeolite loadings (from 1.54 at 0wt % zeolite loading to 3.20 at 20wt % zeolite loading). The increment reaches roughly 52% compared with that of neat PES dense film in the range of our study. This increasing trend of CO_2/CH_4 selectivity with an increase in zeolite loadings is also easily explainable as arising from the effect of the molecular sieving mechanism of zeolite itself. However, according to the literature review it is expected to have better permeability and selectivity at high zeolite loading [11].

Table 2 CO_2 and CH_4 permeability and CO_2/CH_4 selectivity at 3bar with different zeolite loadings in single layer MMMs

Zeolite Loading	CO_2 Permeability (GPU)	CH_4 Permeability (GPU)	CO_2/CH_4 Selectivity
20 wt%	24.97	9.21	3.20
10 wt%	63.96	20.05	3.19
0 wt%	64.57	42.00	1.54

3.4 Comparison of Fabrication for Single and Dual Layer Flat Sheet MMMs on Carbon Dioxide and Methane Separation Performance

By blending PES with zeolite, the properties of the materials expect to give better improvement and higher selectivity as well as to reduce membrane manufacturing cost. In a research conducted by Ismail [12], had shown that the dual-layer structure had more influence on the membranes permeances rather than selectivities of the membrane. Hence, this study aims to improve both permeability and selectivity by fabricating dual layer MMMs with the presence of zeolite 4A in the blend.

Figure 5 and Figure 6 demonstrate the graph of CO2 and CH4 permeability, respectively, and CO2/CH4 selectivity for single and dual layer of mixed-matrix membrane and feed pressure is shown in Figure 7. From the graph, PES-zeolite/PES dual layer MMMs yields very high number of permeability for both pure gases and also the selectivity of CO_2/CH_4. At pressure of 3 bar, the carbon dioxide permeability for dual layer MMMs is above 500 GPU while for single layer is below 50 GPU. The large difference between those two membranes is because of the presence of sub-layer which consists of pure PES for dual-layer MMMs. The sub-layer exhibits less resistance to the gas permeation than the single layer membrane due to the presence of phase separated solid particles and the interconnected pores that surround them. It has been proven by FESEM diagram that zeolites presence in sub-layer of single-layer MMMs cause resistance to gas flowing through the membrane.

Dual-layer MMMs give better performance in term of selectivity too (as shown in Figure 7). At pressure of 3 bar, the CO_2/CH_4 selectivity for dual layer MMMs is 9.63, doubled of the selectivity of single layer MMMs, 3.20. In view of the fact that resistance to transport for a given polymer-penetrant combination is proportional to thickness of membrane, the best methods to enhance the flux without compromising the selectivity is by lessen the thickness.

Compared to PES-zeolite membrane, a single layer MMMs with same zeolite loading, dual layer flat sheet membrane formation is quite less expensive, with minimal loss in permeability and selectivity. Therefore, PES-zeolite/PES dual layer flat sheet of mixed-matrix membrane is the best MMMs produced in this study and can be viewed as new, economical, high performance membrane that is suit for the preparation of gas separation membranes with advance permeation and enhanced properties.

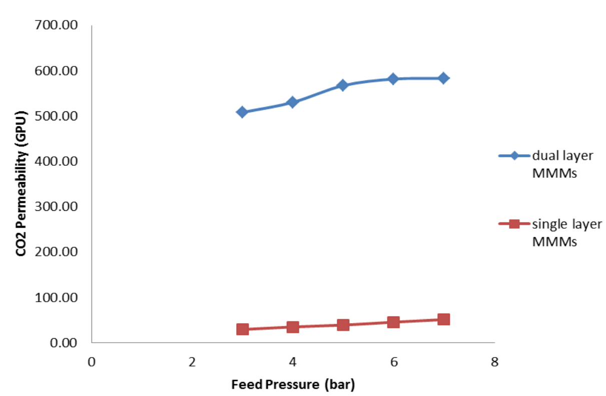


Figure 5 The Permeability of $C0_2$ for single and dual layer MMMs versus the feed pressure

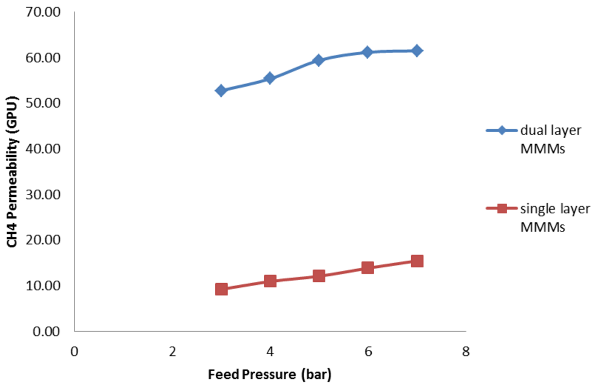


Figure 6 The Permeability of CH4 for single and dual layer MMMs versus the feed pressure

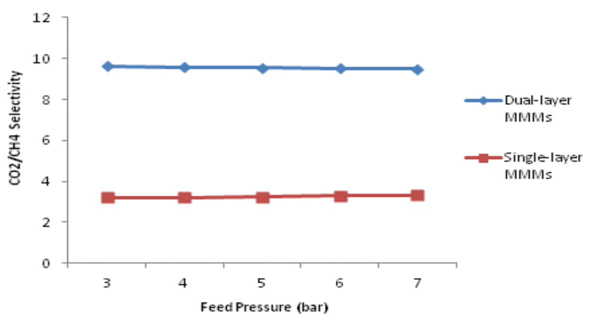


Figure 7 The selectivity of $C0_2/CH_4$ for single and dual layer MMMs against the feed pressure

4.0 CONCLUSION

Flat sheet MMMs by incorporating zeolite 4A into the selected glassy polymer were fabricated and found that the higher the zeolite loading, the higher the selectivity of carbon dioxide separation. In this study, the selectivity of PES-zeolite MMM was increasing up to 25% from 0wt % of zeolite loading to 20wt %. Besides that, the developed flat sheet of dual-layer MMMs with a PES–zeolite 4A mixed-matrix top layer is exhibit better CO_2/CH_4 selectivity. It is 67% higher selective compared with that of asymmetric PES films and PES-zeolite single-layer MMMs.

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